

[On repeating the experiments after the Easter Vacation, an effect was observed which may explain the difference between the value of the wave-length along the wire found in the above experiments and those of Hertz. It happened that the plates after the vacation were placed further from the wall than they had been before, and it was found that the wave-length was much less, being now between seven and eight metres; on moving the plates nearer the wall the wave-length increased, the increase being evidently due to the increase in the capacity of the plate produced by the proximity of the wall. Thus if the distance of the plates from the walls was different in the determination of the wave-length along the wire from what it was in the determination of the wave-length through air, the wave-lengths would not be equal even if the velocity of propagation were the same. I endeavoured to determine the wave-length in air by measuring the distance between the nodes after reflection from a large metal screen, but could not succeed in fixing the position of the nodes with sufficient definiteness to determine the wave-length with any accuracy. The fact, however, that I got a wave-length in the wire the same as that obtained by Hertz through air, is sufficient to show that it is not necessary to suppose that the velocities through the wire and air are different, but that the difference in Hertz's results may have been due to a change in the position of the vibrator relatively to the walls of the room.—May 15.]

II. "Researches in the Chemistry of Selenic Acid and other Selenium Compounds" By Sir CHARLES A. CAMERON, M.D., F.R.C.S.I., V.P.I.C., Professor of Chemistry and Hygiene, R.C.S.I., and JOHN MACALLAN, F.I.C., Demonstrator of Chemistry, R.C.S.I. Communicated by Sir HENRY ROSCOE, F.R.S. Received April 6, 1889.

Although selenic acid was prepared by Mitscherlich so far back as the year 1827, few chemists appear to have studied its properties. This want of interest in selenic acid is rather surprising, seeing that it possesses so close a relationship to sulphuric acid, which is so important a compound. Finding the chemistry of selenic acid so meagre, we resolved to make an investigation of this body, with the view of bringing, so far as we could, its chemistry abreast with that of sulphuric acid, and also in the hope that its study would yield results which might throw additional light on the relations of the latter acid. The following pages contain the results at which we have arrived.

*Preparation of Anhydrous Selenic Acid,  $\text{H}_2\text{SeO}_4$ .*

Selenic acid has hitherto been known only in a dilute form. When heated to about  $260^\circ \text{C}$ . it commences to decompose into selenium dioxide, oxygen, and water, which prevents any further concentration. Berzelius describes it as containing, when of greatest strength, 4 per cent. of water; but since his time it has been obtained in a more concentrated condition by Fabian, who, by evaporating the acid to a temperature of  $265^\circ$ , found it to have a strength of 94.9 per cent., and by placing this acid, while still hot, under the receiver of an air-pump, increased its strength to 97.4 per cent. Sulphuric acid, as is well known, has not been obtained in a perfectly anhydrous state by ebullition—although in its case decomposition does not occur; for when it reaches a strength of about 98.66 per cent. it boils without further change. When, however, an acid of this strength is surrounded with a freezing mixture, the anhydrous acid,  $\text{H}_2\text{SO}_4$ , crystallises out. An attempt was first made to obtain anhydrous selenic acid by similar means. Great care was taken to obtain an acid of pure quality. An examination was specially made for nitric, sulphuric, hydrochloric, and hydrobromic acids. Selenious acid, when present, was removed by diluting with about 30 parts of water, saturating with hydrogen sulphide in the cold, filtering and concentrating on the water-bath. The acid thus treated was then examined for sulphuric acid and found to contain none. A portion of the acid, when ignited, left a residue equivalent to 0.07 per cent. of the anhydrous acid present in the specimen used in the experiments; this was ascertained to consist of neutral sodium selenate, and was, of course, derived from an acid salt, of which it was necessary to take account in the succeeding experiments.

Some of this acid was gradually heated until the temperature rose to  $250^\circ$ . It was next poured into an open dish, and allowed to cool slowly over sulphuric acid, under an exhausted receiver. The strength was then taken with seminormal soda solution, which was specially prepared for those experiments, by making a solution in water of pure caustic hydrate prepared from sodium, and bringing it carefully to the required strength: 11.81 cubic centimetres of soda solution were required for neutralisation by 0.4371 gram of acid, equivalent to 97.75 per cent. of selenic acid, being thus a little stronger than that obtained by Fabian in a similar way.

The acid thus concentrated was then poured into a stout wide glass tube, having one end closed, and the open end fitted with an india-rubber cork, through which passes a glass rod for the purpose of keeping the viscous liquid stirred, and a capillary tube for admission of air, in order to expose the acid to the full atmospheric pressure. The necessity for those precautions in the case of sulphuric acid has

already been fully pointed out by Marignac ('*Annales de Chimie*,' vol. 39, 1853, p. 184), the discordant results arrived at by various observers being probably due to the different conditions under which they worked. The latter precaution is particularly necessary, as we have observed that sulphuric acid occupies less volume in the solid than in the liquid state.

The temperature of the acid was then gradually lowered. Its viscosity increased as it became colder, until at a temperature of  $-51.5^{\circ}\text{C}$ . it was as thick as soft pitch—the tube might be inverted without the acid flowing, and a glass rod could be moved in it only with great difficulty. Still it did not freeze, until after vigorous stirring maintained for a couple of minutes, a crystal appeared, and then the entire mass almost instantaneously crystallised, the temperature rapidly rising. When removed to a warm room, the crystals were rather permanent, and when nearly melted, recrystallisation could easily be induced by exposure to moderate cold so long as any crystal remained, showing that previous to freezing the acid had been in a more or less superfused condition. It was found to be impossible, however, to separate the crystals by draining the liquid portion, as the latter was so viscous that it carried the crystals with it. Under the microscope they were seen to be long prisms.

An attempt was next made to examine the conditions under which selenic acid becomes strengthened in a vacuum, with the object of obtaining, if possible, a more concentrated acid; and the following arrangement was made for the purpose:—The glass receiver of an air-pump was fitted tightly at its neck with an india-rubber cork, through which passed a bent tube, connected horizontally with another and wider tube containing solid potash. This was connected with a wide U-tube, filled with pieces of potash about half an inch long, and kept cool by immersion in a beaker of water. Connexion was then made with a small stout flask containing the selenic acid, and varying in size from 100 to 250 cubic centimetres as required. The potash-tube next the receiver was intended for the purpose of preventing acid fumes from injuring the air-pump, and for the same reason a vessel of potash was placed within the receiver. The air-pump employed gave a very good vacuum; when all the connexions were made, and the pump exhausted, there was often scarcely any appreciable difference in the levels of the columns of mercury in the gauge. For temperatures up to  $100^{\circ}$  the flask containing the acid was heated in a beaker of water; for higher temperatures oil was used. Soon after commencing the experiments it was found necessary to make an arrangement for the purpose of stirring up the viscous acid and exposing fresh surfaces to the vacuum, and the following plan was devised:—A test-tube, which fitted easily the neck of the flask, was shortened by removing evenly a portion of the open end. It was

then inverted and pushed down into the flask, so that when the open end was below the surface of the acid, the closed end extended sufficiently far into the neck of the flask to prevent the tube from being thrown down by the ebullition of the liquid. The vapour given off from the acid within the tube became gradually expanded as the temperature rose, and passed in a stream of bubbles through the acid, keeping it well agitated. The tube also served the purpose of preventing splashing from the boiling acid up into the neck of the small flask.

Some selenic acid, which had been previously partially concentrated, was kept in an open dish on the water-bath for four hours and its strength then determined: 0.6364 gram required for neutralisation 14.72 c.c. of seminormal soda solution, equivalent to 83.68 per cent. of selenic acid—a strength intermediate between a monohydrate and a dihydrate. The acid thus obtained at 100°, under the ordinary pressure of the atmosphere, was stronger than that obtained by Graham from dilute sulphuric acid by heating it to the same temperature in a vacuum until it ceased to lose weight—the dihydrate,  $\text{H}_2\text{SO}_4 \cdot 2\text{H}_2\text{O}$ , remaining showing the greater affinity for water possessed by the latter acid.

Selenic acid, concentrated as above described, was poured into the flask previously referred to, and gradually heated. Weak selenic acid commenced to pass over at 56°, evidenced by the potash liquefying and effervescing, owing to the presence of potassium carbonate which it contained, being the ordinary commercial potash. It was then heated slowly up to 100°, kept at that temperature so long as any acid distilled over, and the strength of the residue taken: 0.9432 gram required for neutralisation 24.10 c.c. of seminormal soda solution, equivalent to 92.44 per cent. of selenic acid. Subsequent to this experiment, acids heated on various occasions to 100° were found to have the following percentages of anhydrous selenic acid:—92.03, 92.08, 93.28, and 93.70; the different results being found due to the varying conditions of the experiments, such as the length of time of heating, the quantity of potash, and its proximity to the acid, the amount of the latter, and the size of the flask containing it.

The acid which had been heated to 100°, was next heated to 150°. At the latter temperature the more or less dilute acid distilling over appeared in the form of dense white fumes resembling those of sulphuric acid. 0.6898 gram of the residue left neutralised 18.42 c.c. of seminormal soda solution, equivalent to 96.58 per cent. of selenic acid. It was again heated to 150°, and kept at that temperature so long as any acid distilled over: 0.417 gram of the residue left neutralised 11.21 c.c. of seminormal soda, equivalent to 97.25 per cent. of selenic acid.

A fresh portion of acid was heated to 155° and kept for some time at that temperature: 0.8045 gram of the residue neutralised 21.72 c.c.

of seminormal soda, showing 97·67 per cent. of selenic acid. It was next heated to 162°, and the strength of the residue taken: 0·7291 gram neutralised 19·72 c.c. of seminormal soda, equivalent to 97·85 per cent. of selenic acid.

The same acid was then heated to 216°, and the residue obtained was allowed to remain in the flask during the night. In the morning it was found to be frozen into a crystalline mass so hard that it was necessary to use a steel chisel in order to remove portions for examination. When dissolved in water and tested it was found to contain some selenium dioxide. Trials were then made to ascertain if a lower temperature would produce a similar result without decomposition of the acid; 180° was found to be sufficient for the purpose, and the following course was finally adopted:—The acid, which had been concentrated on the water-bath as far as possible, was heated gradually in the flask to 100°, and kept at that temperature so long as any acid distilled over, the greater part of the water being thus removed. The U-tube was then disconnected, emptied, and refilled with stick potash. The flask was next heated gradually to 180°, kept at that temperature until no more acid distilled over, and then immediately cooled. A still better arrangement was to use so little acid that it was unnecessary to change the potash. The acid was heated gradually and continuously up to 180°, allowing bubbles to pass slowly through it, as before described. When 180° was reached the potash was watched, and as soon as it ceased to be acted upon the flask was immediately cooled. An hour or less was generally found sufficient time for a small quantity of acid.

A specimen obtained in this way was found, when examined, to be very free from selenium dioxide, a little of it diluted with water and saturated with hydrogen sulphide, merely giving a faint yellow coloration without any precipitate. Another portion was acidified with hydrochloric acid and barium chloride added; on boiling the filtrate with stannous chloride it only became darkened in colour without any precipitation of selenium. 0·6725 gram was taken to estimate the strength: 18·54 c.c. of seminormal soda were required for neutralisation, equivalent to 99·73 per cent. of selenic acid. 0·724 gram of another acid, prepared in a similar way, but which contained rather more selenium dioxide than the last, required for neutralisation 19·94 c.c. of seminormal soda, equivalent to 99·64 per cent. of selenic acid. A portion of a third acid, weighing 0·329 gram, was dissolved in water, barium chloride added, and also hydrochloric acid in order to prevent any selenious acid from precipitating. The resulting barium selenate weighed 0·6337 gram, equivalent to 99·75 per cent. of selenic acid. As has been already mentioned, the acid employed contained an acid potassium selenate equivalent to 0·07 per cent. of neutral sodium selenate found. Taking this into account, and calcu-

lating on the acid with the sodium selenate deducted, the three results become respectively—

I.	II.	III.
99·80	99·71	99·77

The difference between the above results and 100 per cent. must be ascribed partly to the very hygroscopic character of the acid in the anhydrous condition, and consequent slight absorption of moisture during the process of weighing. It is necessary to observe, however, that in making the above calculations, and all through in this paper, 78·87 has been adopted as the atomic weight of selenium, the number given by Meyer and Seubert in their 'Recalculations of the Atomic Weights.' If 78·80, the number given in Clarke's 'Recalculations,' be taken, the three results become—

I.	II.	III.
99·75	99·66	99·72

Petersson and Ekman state that the results of a great many analyses show that the most probable atomic weight of selenium is 79·08 ('Berichte Deutsch. Chem. Gesell.,' vol. 9, p. 1210). If this number be taken, the above percentages become respectively—

I.	II.	III.
99·94	99·85	99·91

The results arrived at from the foregoing experiments lead to the conclusion that at 180° in a vacuum, selenic acid parts with all combined water, and remains as the anhydrous acid,  $\text{H}_2\text{SeO}_4$ .

It may be well here to summarise the precautions necessary to be taken in preparing the anhydrous acid, so far as we have ascertained them. They are briefly as follows:—To use for the purpose an acid as pure as possible, to have a thoroughly good vacuum, to avoid too high or prolonged heating, and to keep a sufficient quantity of solid potash in close proximity to the acid all through—which may be arranged by using a small flask, and having the tube leading from it short and wide.

#### *Properties of Anhydrous Selenic Acid.*

Anhydrous selenic acid is a white crystalline solid melting at 58° to a colourless oily-looking liquid. When thoroughly melted it remains in a superfused state, and usually requires to be cooled to about 5° with constant stirring before it again freezes. The temperature then rises rapidly to 58°, and remains stationary until complete solidification of the acid has taken place. When at rest it can be cooled lower than 5° without freezing, and it will remain in a stoppered bottle for months, and during frosty weather, in a liquid condition.

It instantly solidifies at any temperature below  $58^{\circ}$  if a crystal of the solid acid be dropped into it, and it freezes sometimes at ordinary temperatures when rubbed with a sharp piece of glass or with the point of a pipette. It thus exhibits the property of superfusion in a remarkable degree, and to a greater extent than anhydrous sulphuric acid, which, according to Marignac, possesses eminently the property of superfusion ('*Annales de Chimie*,' vol. 39, 1853, p. 184). Its melting point,  $58^{\circ}$ , is higher than that of anhydrous sulphuric acid,  $10.5^{\circ}$ , but lower than that of telluric acid, which may be heated nearly to redness without melting.

Anhydrous selenic acid crystallises in long interlacing hexagonal prisms. In an impure condition from the presence of selenium dioxide and other substances, its melting point is lowered, and under those circumstances it is sometimes deposited slowly and spontaneously in the form of double pyramids, many of them intersecting in pairs.

Although much has been written upon the freezing-point of sulphuric acid, but little information appears to be published regarding its crystalline form. It is stated, however, in Graham's '*Chemistry*,' vol. 1, that the most concentrated acid, when frozen, often yields regular six-sided prisms of a tabular form. Chaptal describes the crystals as being six-sided prisms terminating in pyramids with six faces. Both accounts agree in placing them in the hexagonal system. In order to see if the appearance of the crystals agreed with either of the above descriptions, some sulphuric acid was strengthened by boiling for some time, and then cooled down until it froze. The crystals obtained were found to be long six-sided prisms ending in pyramids, as described by Chaptal, and no prisms of a tabular form were observed. It is thus interesting to find that both anhydrous sulphuric and selenic acid crystallise in prisms in the hexagonal system, but it remains doubtful whether or not they are strictly isomorphous.

Selenic acid in the anhydrous condition possesses a powerful affinity for water, absorbing it quickly from the atmosphere. Their combination is attended with contraction and considerable evolution of heat, but less so than in the case of water and sulphuric acid. Like the latter, it disintegrates and blackens many organic substances, such as cork, india-rubber, &c. From others it withdraws the elements of water; thus, alcohol heated with it yields ethylene, and glycerine, acrolein. On cellulose it has an action similar to that of strong sulphuric acid, paper being converted by it into a tough parchment-like substance. For this reason it should not be filtered through filtering paper, except when cold and very dilute. Iodine dissolves in the superfused acid when heated, forming a brown-coloured solution. It is acted on violently by pentachloride of phosphorus in the cold—a reaction which we are at present examining. Oxychloride of

phosphorus also acts strongly upon it when warmed slightly, the reaction being attended with copious evolution of gas and reduction apparently to lower compounds. Selenium dioxide dissolves in it when heated, but the greater part crystallises out again in the cold. There is no evidence of formation in this way of an acid analogous to hyposulphuric acid,  $\text{H}_2\text{S}_2\text{O}_6$ . The crystals of the solid acid dissolve in strong sulphuric acid, and also in Nordhausen acid.

The specific gravity of the superfused acid, taken with a Sprengel tube at  $15^\circ$ , was found to be 2.6083. The specific gravity of the solid acid was taken in pure benzene of specific gravity 0.8851, which is not acted upon by it in the cold, and in which it is insoluble. As might be expected, it at once blackens commercial benzene. Its specific gravity, taken in this way, proved to be 2.9508 at  $15^\circ$ . It thus resembles anhydrous sulphuric acid in being denser in the solid than in the liquid state. The specific gravity of the liquid acid is much greater than that of anhydrous sulphuric acid, 1.8384; and on the other hand the specific gravity of the solid acid is less than that of anhydrous telluric acid, which is stated by F. W. Clark to be 3.425 at  $18.8^\circ$  ('American Journal,' vol. 14, 1877, p. 281; vol. 16, 1878, p. 401).

*Monohydrated Selenic Acid: its Preparation and Properties.*

Some selenic acid, which had been concentrated on the water-bath, was heated for some time in a vacuum at  $100^\circ$ , and its strength determined: 0.7858 gram neutralised 20.00 c.c. of seminormal soda solution, equivalent to 92.08 per cent. of selenic acid. The acid so prepared was diluted with sufficient water to reduce its strength to 88.96 per cent., corresponding to a monohydrated acid,  $\text{H}_2\text{SeO}_4 \cdot \text{H}_2\text{O}$ . It was then poured into a wide tube and its temperature gradually lowered, the same precautions being taken as to stirring and admission of air as were adopted previously in freezing out the anhydrous acid. Its viscosity increased with the fall in temperature, until at  $-32^\circ$  it froze into a mass of crystals. These were melted and re-crystallised several times, and the resulting product examined.

A few of the crystals obtained were long needles, but most of them were large and broad, having a general aspect to which the term "glacial" might be applied appropriately, but differing in appearance under the microscope from those of glacial sulphuric acid.

Its melting point was found to be  $25^\circ$ . Like glacial sulphuric acid, and also like anhydrous sulphuric and anhydrous selenic acid, when once melted it exhibits the property of superfusion, and to as great an extent as the last-mentioned acid, since it may be cooled to more than  $50^\circ$  below its melting point, with constant stirring, before it again freezes. When frozen it remains quite solid at ordinary temperatures; but if the bottle containing it be removed to a warm



room, or much handled, it commences to melt. Like the anhydrous acid, it at once freezes at any temperature below its melting point when a crystal of the same acid is dropped into it. It resembles the anhydrous acid also in having a melting point much higher than sulphuric acid of the same strength, that of glacial sulphuric acid being given by Pierre and Puchot as  $7.5^{\circ}$ , by Jacquelin as  $8^{\circ}$ , and by Marignac as  $8.5^{\circ}$ . It resembles the latter acid in having a melting point lower than its anhydrous acid, but while the difference is about  $2.5^{\circ}$  in the case of sulphuric acid, the melting points of the two selenic acids differ by  $33^{\circ}$ . In the following table their melting points are compared:—

	Anhydrous.	Monohydrated.
Sulphuric acid.....	$10.5^{\circ}$	$8^{\circ}$
Selenic acid.....	$58.0$	$25$

It may be well to state here that  $0^{\circ}$  is given erroneously in several chemical works as the melting point of anhydrous sulphuric acid. Marignac, the most recent investigator who has studied the subject, assigns the temperature  $10.5^{\circ}$  as its true melting point.

The superfused monohydrated selenic acid has a specific gravity of 2.3557 at  $15^{\circ}$ . That of the solid acid was taken in pure benzene, in which it is insoluble, and on which it is without action at ordinary temperatures, even after standing all night. A portion of the liquid acid was poured into the specific gravity bottle, a crystal dropped into it, and the acid, having become firm and cold, weighed, and the bottle filled with benzene. The specific gravity was found to be 2.6273 at  $15^{\circ}$ . It thus resembles the anhydrous acid in being denser in the solid than in the liquid state; while melting, the crystals sink rapidly in the liquid portion.

This acid commences to boil at  $205^{\circ}$ , the acid vapour given off being at first very weak, but it increases in strength with the rise in temperature. A more dilute acid gives off water only until the temperature reaches  $205^{\circ}$ . Dilute sulphuric acid is stated to behave in a similar manner, giving off nothing but water until the boiling point reaches  $205$ — $210^{\circ}$ , at which temperature it has the strength of the monohydrated acid,  $\text{H}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ .

The ease with which an acid of this strength can be obtained and crystallised, supplies a means of separating impurities from selenic acid, all that is necessary to do being to boil a dilute acid until the temperature reaches  $205^{\circ}$ , cool, and drop in a crystal from an acid already frozen; the resulting crystals can then be melted and recrystallised.

It may be well here to draw attention to the conflicting statements which are made in various works regarding the crystalline form of glacial sulphuric acid. Watts's 'Dictionary,' vol. 5, and Richter's

'Inorganic Chemistry,' state that it crystallises in six-sided prisms; but in several chemical works the crystals are described as rhombic prisms, while Pelouze and Fremy mention that it forms large transparent crystals which are rhomboidal prisms. The crystalline form is thus referred to three different systems. The first description is probably copied by mistake from that of the anhydrous acid. The most recent investigators of the point are Jacquelin ('Annales de Chimie,' vol. 30, 1850, p. 343), and Pierre and Puchot ('Annales de Chimie,' vol. 2, 1874, p. 164). The latter say that the crystalline form appeared to them to be the oblique rhomboidal prism, and that they obtained the crystals, some very large, others thin and very long. Jacquelin describes them as being oblique prisms very inclined and very large; and states that he obtained them, by a rather slow crystallisation, distinctly oblique and very short, and by a quick crystallisation, in very long oblique prisms.

*The Existence of higher Hydrates.*

A portion of dilute selenic acid was concentrated on the water-bath and its strength taken: 0.8603 gram neutralised 19.48 c.c. of semi-normal soda solution, equivalent to 81.92 per cent. of selenic acid. The acid so prepared was diluted with sufficient water to reduce its strength to 80.11 per cent., corresponding to a dihydrated acid,  $\text{H}_2\text{SeO}_4 \cdot 2\text{H}_2\text{O}$ , and its temperature then gradually lowered. When kept at  $-51^\circ$  for some time it became as viscous as thick syrup, but did not freeze. The last acid was then diluted to a strength of 57.32 per cent. of selenic acid, corresponding to a hydrate of the composition  $\text{H}_2\text{SeO}_4 \cdot 6\text{H}_2\text{O}$ . The acid thus prepared did not freeze when kept at  $-49^\circ$ , and was quite liquid at that temperature.

Although no proof of the existence of higher hydrates than the monohydrated acid was obtained in the foregoing experiments, it appears probable that a dihydrated acid, and perhaps other hydrates, are capable of existing. Sulphuric and telluric acid have both been obtained as dihydrates. Considerable heat is evolved when monohydrated selenic acid is mixed with sufficient water to reduce its strength to that of a dihydrated acid. When the latter is further diluted, there is an additional slight evolution of heat. It is probable that as the freezing point of monohydrated selenic acid is considerably below that of the anhydrous acid, so the freezing point of a dihydrated acid is still lower. In order to get an approximate idea of the amount of water which anhydrous selenic acid absorbs, a portion weighing 0.9776 gram was placed on a watch-glass protected from dust, but with free access of air. After twenty-four hours the acid weighed 2.0284 grams, showing an absorption in that time of between 8 and 9 molecules of water by 1 molecule of anhydrous acid. Another portion weighing 0.4416 gram was exposed until it ceased to

absorb water; the acid then weighed 1·8152 grams, indicating absorption of rather more than 25 molecules of water by 1 molecule of anhydrous acid. Having arrived at this stage, it commenced to give off a little of the water which it had previously taken up, but the weather became warmer just at this period, so that probably the above amount does not represent the total absorption of which the acid is capable. It is less, however, than the amount taken up by the molecule of sulphuric acid, which is variously stated at from 80 to 100 molecules of water.

*The Conditions which affect the Freezing Points of Selenic Acid and Sulphuric Acid.*

It has long been recognised that in order to determine the melting point of a chemical compound with accuracy it is necessary, by crystallisation or other means, to obtain it in a pure condition. The necessity for such a precaution is well shown in the case of the oxides and acids of sulphur and selenium. An example taken from the former class of bodies is furnished by sulphuric anhydride. Up to a comparatively recent date great diversity of opinion prevailed regarding the melting point of this substance until Weber showed that, as hitherto examined, it had usually contained a minute quantity of water, which had the effect of altering its melting point, crystalline form, and other properties. Sulphuric acid supplies another instance of a similar effect. Its melting point in the anhydrous condition is  $10\cdot5^{\circ}$ , while that of the monohydrated acid is  $8^{\circ}$ ; yet commercial sulphuric acid has usually been found to remain liquid above a temperature of  $-30^{\circ}$  or  $-40^{\circ}$ , and it is stated in some chemical works that by addition of a little water to the commercial acid its freezing point has been lowered to  $-80^{\circ}$ ; but it is not mentioned whether or not this occurred in closed or open vessels. A still more striking example of the influence of want of purity upon the melting point is afforded by selenic acid. In the anhydrous state it melts at  $58^{\circ}$ , but a slightly dilute acid, as we have found, was frozen only when a temperature of  $-51\cdot5^{\circ}$  was reached, showing a fall of  $109\cdot5^{\circ}$ , and probably further dilution would be attended by a still greater reduction of the freezing point. The depression of the freezing point can be due only partly to superfusion since the super-fused anhydrous acid freezes at about  $5^{\circ}$ . The monohydrate present in the dilute acid therefore exerts an influence in lowering the freezing point of the anhydrous acid, and also its melting point. An analogous action probably occurs in the case of some metallic salts, which, although without apparent chemical action upon each other, have a lower fusing point when mixed than when heated separately. A consideration of the foregoing facts leads to the conclusion that *dilute selenic acid having a strength greater than 88·96 per cent. contains the*

*anhydrous and also the monohydrated acid existing in a superfused state, and exerting a solvent action upon each other.* In the case of sulphuric acid a similar action evidently occurs. The effects of agitation and of alteration of pressure upon the freezing points of the above acids have already been referred to.

*The Method used in Freezing Selenic Acid.*

Liquefied sulphur dioxide was poured into a thick glass tumbler, holding about half a litre, fitting into a somewhat wider and deeper cylindrical gas jar, which served to retain any of the dioxide splashed from the interior vessel, the whole being imbedded deeply in a considerable quantity of cotton wadding contained in a wooden box. A rapid current of air was driven through the sulphur dioxide, the air being first dried by means of sulphuric acid and then cooled by passing through a leaden worm surrounded by a mixture of salt and pounded ice, or less effectively, sodium sulphate and hydrochloric acid. Any desired degree of cold within limits could easily be maintained by regulating the current. When the outside air was at  $0^{\circ}$ , about half a kilogram of sulphur dioxide was found sufficient for more than two hours' use, evaporation taking place but slowly at the low temperature reached, the latter, measured with an alcohol thermometer, falling below  $-50^{\circ}$  C. In warmer weather nearly as low a temperature was obtainable, but consumption of the sulphur dioxide was much more rapid. No arrangement of freezing mixtures produced nearly so low degrees of cold as were attained in the above manner. Doubtless when a supply of dry snow is available, and the weather is very cold, so that the apparatus and materials used can be well cooled down previous to mixing, a very low temperature is obtainable by ordinary freezing mixtures, but those conditions are not often to be met with in these climates. On the other hand, sulphur dioxide is cheap and easily procurable, and convenient when used in the manner described.

*The Specific Gravities of the Higher Strengths of Selenic Acid.*

The specific gravities of selenic acid for the higher strengths, taken in the liquid state at  $15^{\circ}$ , are given in the following table. The most concentrated acid, of 99.73\* per cent. strength, has been referred to under the head of the preparation of the anhydrous acid; its specific gravity, 2.6083, was taken while in the superfused condition. The next acids down to 94.74 per cent. were obtained by diluting that of 99.73 per cent. The acid having a strength of 93.70 per cent. was obtained by heating dilute acid in a vacuum at

\* 99.73 per cent. of selenic acid, acid sodium selenate, equivalent to 0.07 per cent. of neutral sodium selenate, and 0.20 per cent. of water (Se being = 78.87).

100°, and it supplied the following strengths, down to 82·52 per cent. by progressive dilution. That of 81·73 per cent. was prepared by concentration on the water-bath, and the remaining four by dilution of the latter. Neither the acid heated in a vacuum, nor that which was kept on the water-bath, contained any trace of selenious acid.

Table I.

Percentage of anhydrous selenic acid.	Specific gravity.
99·73	2·6083
99·08	2·5993
98·68	2·5901
98·16	2·5790
97·37	2·5676
96·97	2·5595
96·16	2·5424
94·74	2·5105
93·70	2·4852
92·83	2·4534
91·59	2·4218
90·06	2·3863
89·20	2·3642
88·55	2·3402
87·34	2·3158
86·60	2·2946
85·67	2·2712
84·59	2·2463
83·82	2·2196
82·52	2·1878
81·73	2·1694
80·86	2·1438
79·99	2·1213
79·06	2·0940
73·43	1·9659

Table II is calculated from Table I, and gives specific gravities interpolated from equal increments of strength. It will, perhaps, be found most convenient for purposes of calculation, and for showing the relation of the rate of increase of specific gravity to that of the strength.

Table II.

Percentage of anhydrous selenic acid.	Specific gravity.
99·73	2·6083
99·50	2·6051
99·00	2·5975
98·50	2·5863
98·00	2·5767
97·50	2·5695
97·00	2·5601
96·00	2·5388
95·00	2·5163
94·00	2·4925
93·00	2·4596
92·00	2·4322
91·00	2·4081
90·00	2·3848
89·00	2·3568
88·00	2·3291
87·00	2·3061
86·00	2·2795
85·00	2·2558
84·00	2·2258
83·00	2·1946
82·00	2·1757
81·00	2·1479
80·00	2·1216
79·00	2·0922
73·50	1·9675

The rate of increase of specific gravity is not uniform for equal increments of strength. It diminishes as the strength increases, as in the case of sulphuric acid, but not regularly. The diminution is very marked at the highest strengths. When sulphuric acid has arrived at the greatest strength attainable by ebullition—98·66 per cent.—its specific gravity is stated to decrease until the anhydrous acid,  $\text{H}_2\text{SO}_4$ , is reached. Selenic acid behaves dissimilarly in this respect; the increase of its specific gravity, although not uniform, is maintained throughout.

Berzelius ('*Traité de Chimie*,' 1830) mentions that selenic acid of 95·9 per cent. strength has a specific gravity of 2·6. Fabian gives 2·609 as the specific gravity of an acid of 94·9 per cent. strength, and 2·627 for an acid of 97·4 per cent. It will be seen that these results do not agree, nor are they consistent with those we have obtained. If values for the strengths mentioned be calculated from the foregoing

tables, an acid of 95.9 per cent. will be found to have a specific gravity of 2.5366, while the specific gravities of 94.9 per cent. and 97.4 per cent. acids will be respectively 2.5141 and 2.5680, being less than those assigned above. Furthermore, the difference between the two specific gravities given by Fabian is much less than we find between two acids differing by 2.5 per cent. The most probable explanation of the discrepancy is that the acids which gave the above results contained sufficient selenium dioxide to raise their specific gravities appreciably. It may be shown that the effect of the development of selenium dioxide in selenic acid is to increase the specific gravity relatively to the acidity. In the acids above-mentioned, selenium dioxide would exist as such, and not as selenious acid, owing to dissociation of the latter at a temperature below those at which the acids were formed, and the weak affinity for water possessed by the resulting dioxide. Clausnizer ('*Liebig's Annalen*,' vol. 196, 1879, p. 265) gives the specific gravity of selenium dioxide at 15.3° as 3.9538. We have also recently taken its specific gravity, and are in a position to confirm his result. It is thus more than one and a half times as dense as the strongest selenic acid. C. Blarez ('*Comptes Rendus*,' vol. 103, 1886, pp. 804—806) has examined the saturating power of selenious acid. He finds that it is monobasic with cochineal or methyl-orange. With litmus, it is monobasic to ammonia, lime, strontia, and baryta, but with soda or potash the litmus only becomes blue-violet when about 1.5 equivalent of alkali is added. We have obtained a like result with soda or potash and litmus. When one equivalent of acid is saturated, there is a distinct change in the colour of the litmus, so that in the absence of other acids it might be used as an indicator for selenious acid. Taking 1.5 equivalent of alkali as the limit, the molecule of selenium dioxide in solution will have a less saturating power than that of selenic acid in the ratio of 2:1.5. This will be partly counterbalanced by the higher molecular weight of the latter, but the final effect of the substitution of selenium dioxide for selenic acid will be to reduce the acidity. A gravimetric method, by which selenium dioxide would be oxidised and estimated as selenic acid, would also show a less acidity compared with the specific gravity than if the pure acid were used, but not to the same extent as when a volumetric process is employed for estimating the strength.

#### *The Action of Heat upon Selenic Acid.*

*Action of Heat in a Vacuum.*—The effect of heating dilute selenic acid in a vacuum up to 180° has already been described—dilute acid distils until that temperature is reached, when the anhydrous acid remains.

The result of further heating is merely for a time to raise the

temperature; the acid does not distil in the anhydrous condition. At about  $200^{\circ}$  it begins to decompose slowly, and at higher temperatures rapidly, into selenium dioxide, oxygen, and water. The latter serves to dilute a portion of the remaining acid, which then at once distils. In order to examine the effect of distilling the anhydrous acid destructively in a vacuum, a portion was heated in a flask connected with a condensing arrangement until rapid decomposition took place. The residue always consisted of a mixture of anhydrous selenic acid with selenium dioxide, the proportion of the latter increasing with the rise of temperature and length of time of heating. The former was proved to be present by dropping in a crystal of anhydrous acid, when the liquid froze, and it also gave a coloration in the cold with the selenium test for the same acid which will be described hereafter. A portion which had been distilled for some time left a residue of which 0.7107 gram neutralised 18.50 c.c. of seminormal soda solution, using litmus as indicator, equivalent to 94.27 per cent. of acid calculated as selenic—a result which might be expected, owing to the influence of the selenium dioxide in diminishing the acidity, as has been already pointed out. The distillate consisted of selenium dioxide mixed with selenic acid. The latter was in a dilute state, since it would not solidify on addition of a crystal of anhydrous acid, nor would it respond to the selenium test: 0.4703 gram neutralised 11.11 c.c. of seminormal soda solution, equivalent to 85.46 per cent. of acid calculated as selenic. Taking into account the diminution of acidity caused by the selenium dioxide, it is evident that a very concentrated, although not anhydrous, acid distils over.

*Action of Heat under ordinary Pressures.*—When dilute selenic acid is boiled at ordinary pressures nothing but water is evolved until  $205^{\circ}$  is reached, at which temperature it has the composition of the monohydrated acid. In these respects it behaves like dilute sulphuric acid. After passing  $205^{\circ}$  the distillate contains at first mere traces of selenic acid, but its strength gradually increases. A portion of acid distilled between  $205^{\circ}$  and  $227^{\circ}$  yielded a distillate of which 0.6826 gram neutralised 0.10 c.c. of seminormal soda solution, equivalent to 0.53 per cent. of selenic acid. On further heating from  $227^{\circ}$  to  $260^{\circ}$  a distillate was obtained, of which 0.3818 gram neutralised 0.32 c.c. of seminormal soda solution, equivalent to 3.03 per cent. of selenic acid. At the latter temperature the acid commenced to distil over in white fumes. 0.6878 gram of the residue left at  $260^{\circ}$  neutralised 17.76 c.c. of seminormal soda solution, equivalent to 93.41 per cent. of selenic acid. At higher temperatures a portion of the acid is decomposed, the distillate being kept weak by the water continuously set free in the decomposition; and at still higher temperatures much selenium dioxide also distils over. A portion of acid



which commenced to boil at  $235^{\circ}$  was heated until the temperature rose to  $325^{\circ}$ : 2.1542 grams of the distillate neutralised 3 c.c. of seminormal soda solution, equivalent to 5.04 per cent. of selenic acid. The residue was then further heated until the greater part of the acid was decomposed and the strength of the distillate taken: 1.6176 grams neutralised 16.5 c.c. of seminormal soda solution, equivalent to 36.90 per cent. of acid calculated as selenic, but much of the acidity was due to selenious acid, a large amount of which was present in the distillate. It is thus seen that the acid which distils under ordinary pressures is always highly dilute.

When anhydrous selenic acid is strongly heated under ordinary pressures a portion of it is decomposed into selenium dioxide, oxygen, and water, the latter serving to dilute the remaining acid. It will then no longer solidify on addition of a crystal of the anhydrous acid. After further heating it becomes sufficiently dilute to distil over in the manner already described. It is instructive to compare with this the action which takes place in the case of anhydrous sulphuric acid. Marignac found ('*Annales de Chimie*,' vol. 39, 1853, p. 184), that the latter when heated gives off sulphuric anhydride until the remaining acid is reduced to the same strength as that yielded by a more dilute acid on prolonged ebullition—about 98.66 per cent. In the case of selenic acid the anhydride is evidently unable to exist free at elevated temperatures, but breaks up into selenium dioxide and oxygen.

It is worthy of note that a remarkable coincidence exists between the temperature at which selenic acid is decomposed and that at which selenium dioxide sublimes. The latter is not stated very definitely in any of the chemical text-books; we have found, however, that at  $280^{\circ}$  rapid sublimation takes place, while at  $250^{\circ}$  volatilisation proceeds slowly. When selenic acid is kept for some time at the latter temperature it is always found to contain traces of selenium dioxide, while at  $280^{\circ}$  decomposition proceeds with rapidity. It is probable that a connexion exists to a considerable extent between the phenomena, and that the explanation of the coincidence may be that the comparatively weak affinities which bind the molecule of selenic acid are unable to prevent its disruption when once a temperature is reached at which the tendency of its constituents to separate is aided by the expansion attending a change to the gaseous condition. We have seen that both phenomena are affected by the temperature; they are also dependent to some extent upon the pressure. Anhydrous selenic acid commences to dissociate in a vacuum at about  $200^{\circ}$ . We found that when selenious acid was heated under similar circumstances water was quickly evolved, and after prolonged heating of the residue a distinct white ring of selenium dioxide was deposited on the cold portion of the neck of the flask.

*The Action of Sulphur upon Selenic Acid.*

When powdered sulphur is mixed with liquid anhydrous selenic acid there is no action in the cold, but if the mixture is heated to  $63^{\circ}$  the sulphur dissolves in the acid with production of an exceedingly deep indigo-blue colour. There is some action, but slight, at  $58^{\circ}$ . The body which is produced is very unstable, since it begins to decompose at the temperature at which it is formed, with evolution of sulphur dioxide, and reduction of the selenic acid to selenious acid. If water is added when the colour has first developed, sulphur is deposited in soft yellow flakes; but after decomposition has commenced, the addition of water throws down red selenium chiefly, owing to the reaction between the sulphurous and selenious acids which are formed.

A similar action has long been known to occur between sulphur and sulphuric acid. In 1804 Bucholz (Gehlen's 'Neues Journal der Chemie,' vol. 3, p. 7) discovered that sulphur dissolved in the latter acid with the formation of a blue colour, the sulphur being re-precipitated on addition of water. This reaction was subsequently investigated by Vogel, Schweigger, Berzelius, Wach, and Stein, and in 1875 Weber succeeded in isolating the blue compound (Poggendorff's 'Annalen,' vol. 156, p. 531), and discovered it to be a sesquioxide of sulphur,  $S_2O_3$ , but very unstable, decomposing at ordinary temperatures with evolution of sulphur dioxide.

*The Action of Selenium upon Selenic Acid.*

A reaction takes place between selenium and anhydrous selenic acid in the cold. The selenium dissolves in the acid with production of an intense and beautiful green colour. The presence of a minute quantity of water prevents the colour from developing fully until the acid is warmed. The acid is capable of dissolving a considerable quantity of selenium. If kept in a closed vessel the colour thus produced is very permanent, being unaffected for months during summer weather, but if the acid be heated to  $75^{\circ}$  the colour disappears, and the selenic acid is found to be partly reduced to selenious acid. Addition of water, when the colour has developed, throws down a voluminous red precipitate of selenium; and exposure to the air in an open vessel for a few minutes is sufficient, from the same cause, to change the green colour to red. It will be shown hereafter that this green colour is probably caused by the formation of a new oxide of selenium. Its production with the anhydrous acid affords a test for the latter, which we have already made use of in the examination of the effect of heat upon selenic acid.

In 1827 Magnus found that selenium was dissolved by strong sulphuric acid, with development of a green colour, and was re-precipitated on addition of water. Berzelius and Fischer subsequently

investigated the reaction, and in 1875 Weber (Poggendorff's 'Annalen,' vol. 156, p. 545) isolated the green compound, and found it to be a sulphoxide of selenium,  $\text{SeSO}_3$ . The colour given by selenium with sulphuric acid is a dark green, not so bright as that which it produces with selenic acid.

*The Action of Tellurium upon Selenic Acid.*

Like selenium, tellurium reacts upon anhydrous selenic acid in the cold, but with production of a purple-red colour. Even when the acid is not perfectly anhydrous, it will still give a coloration in the cold. The compound thus formed is probably very unstable, since the colour disappears at so low a temperature as  $19^\circ$ , the selenic acid being partly reduced to selenious acid. If water is added when the colour has developed, tellurium is thrown down in sooty flakes, and exposure to moist air produces the same effect.

Tellurium reacts in a similar manner with strong sulphuric acid, with development of a red colour, and re-precipitation on addition of water. This was first observed by Müller von Reichenstein. In 1789 the same reaction was investigated by Klaproth, and afterwards by Magnus and Fischer. The red compound was isolated by Weber in 1882 ('Journal für Praktische Chemie,' vol. 25, p. 218), and soon afterwards independently by Divers and Shimosé ('Journal of the Chemical Society (Transactions),' vol. 43, p. 319), and was ascertained to be tellurium sulphoxide,  $\text{TeSO}_3$ .

*Comparison of Sulphoxides with Selenoxides.*

The coloured compounds first formed by the action of sulphur, selenium, and tellurium upon sulphuric acid were subsequently produced by the action of the same bodies upon sulphuric anhydride, and were isolated by forming them in the latter manner, and then removing the excess of anhydride. As has been already mentioned, they were found to be sulphoxides having the composition respectively  $\text{SSO}_3$ ,  $\text{SeSO}_3$ , and  $\text{TeSO}_3$ . Considering the similarity of the reactions which produce them, and of the decompositions to which they are liable, it is very probable that the coloured bodies formed with selenic acid are selenoxides, analogous to the sulphoxides already known, the sulphur in the latter being replaced by selenium. A comparison of the formulæ of the two series of bodies as represented in the following table, leads to some interesting considerations:—

Colour of compound.	Sulphoxides.	Selenoxides.
Blue	$\text{SSO}_3$	$\text{SSeO}_3$
Green	$\text{SeSO}_3$	$\text{SeSeO}_3$
Red	$\text{TeSO}_3$	$\text{TeSeO}_3$

The green body formed by the action of selenium upon selenic acid is, in all probability, a new oxide of selenium, having the composition  $\text{Se}_2\text{O}_3$ , analogous to the sesquioxide of sulphur formed by the action of sulphur upon sulphuric acid.

The colour of the above compounds appears to be almost entirely due to the element which is added on to the anhydride; the sulphur or selenium in the residual portion of the molecule has scarcely any effect upon the colour.

The green body  $\text{SeSO}_3$  must be isomeric with the blue compound  $\text{SSeO}_3$ , and consequently the atoms of sulphur and selenium in each of these bodies must occupy dissimilar positions in the molecule.

#### *The Possible Existence of Selenic Anhydride.*

A consideration of the foregoing facts leads to the conclusion that selenic anhydride, which has not up to the present time been obtained, is yet capable of existing in a free condition. Just as the sulphoxides are direct addition compounds of sulphur, selenium, and tellurium respectively, with sulphuric anhydride, so the selenoxides must be regarded as addition compounds of the elements mentioned, with selenic anhydride. It is difficult to conceive that bodies so constituted are capable of existing free, and that the anhydride is unable to do so. On the other hand, it is probable that it dissociates at a comparatively low temperature, but one that is higher than  $75^\circ$ —the highest temperature at which the most stable of the selenoxides has been as yet found to exist. Selenious anhydride is always obtained, and not selenic, under similar conditions to those which produce sulphuric anhydride, and involving a high temperature.

We have examined the action of heat upon various selenates. Those selected for the purpose were the selenates of antimony, bismuth, platinum, lead, and silver, and also ferric and mercuric selenates. In no instance was selenic anhydride obtained, but selenious anhydride was evolved in all cases when the above selenates were strongly heated.

Von Gerichten ('Liebig's Annalen,' vol. 168, 1873, p. 214) endeavoured to form selenic anhydride in a similar manner to that by which sulphuric anhydride is usually obtained—by leading a mixture of oxygen and the vapour of selenious anhydride through red-hot platinum sponge. He states that in one experiment a white deposit was obtained which consisted partly of selenious anhydride, but probably also contained selenic anhydride, since it dissolved in water with a hissing sound, and the solution was found to contain selenic acid. In subsequent experiments a decidedly negative result was obtained, since only selenious anhydride was found in the product.

In order to examine if selenic anhydride is produced in the manner just described, the following experiments were made:—

Some platinum sponge was introduced into a combustion tube, and a quantity of selenious anhydride placed behind it. The platinum sponge was kept at a red heat, and the selenious anhydride was also heated until it sublimed. Oxygen, which was first dried by passing through a series of tubes containing calcium chloride and sulphuric acid, was led through the platinum sponge, carrying the vapour of the selenious anhydride with it. A white deposit formed in front of the platinum sponge, which, on examination, was found to consist solely of selenious anhydride.

The experiment was repeated, substituting selenium for selenious anhydride. The vapour of the selenium, on passing through the platinum sponge, was oxidised to selenious anhydride, but no selenic anhydride was formed.

The next experiment was similar to the first, but platinum black was substituted for platinum sponge. As before, only selenious anhydride was deposited.

In the next experiment selenious anhydride was mixed with platinum sponge, and placed within a tube arranged in such a way that it could be placed in an oil-bath. The temperature was then raised gradually to  $250^{\circ}$ , oxygen being led through continuously. At the temperature mentioned a sublimate formed, and this, as well as the platinum sponge, was treated with water and tested, but no selenic acid was found.

The next experiment was similar to the last, except that the selenious anhydride was mixed with platinum black instead of platinum sponge, but, as before, nothing but selenious anhydride was obtained.

As may be seen from the above experiments, we have been unable to confirm the observation made by von Gerichten.

We have found that oxygen in the active condition is unable to oxidise selenious anhydride. Oxygen, which was first passed through a series of drying tubes, was ozonised by means of a Houzeau's ozoniser, and then led slowly through a tube containing selenious anhydride for three hours and a half. At the end of that time the tube was disconnected, the ozone displaced by a current of dried air, and the contents of the tube dissolved in water and tested for selenic acid, but no trace of it was detected.

#### *The Selenates of Antimony, Bismuth, and Platinum.*

In the examination of the action of heat upon selenates, the three above mentioned were included. We have been unable to find any published account of these, and accordingly give here a short description of them.

*Antimonious Selenate.*—This body was formed by heating metallic

antimony with selenic acid until it dissolved, and then continuing the heating until the excess of acid was driven off. It forms a white crystalline mass, which under the microscope is seen to consist of minute prisms. It is not very soluble in acids, but on boiling with selenic acid for some time it dissolves slightly, but apparently without formation of an acid salt, as the crystals deposited on evaporating the solution have the same shape and size as the original salt. It is not decomposed on boiling with water, nor is it soluble; if, however, the excess of selenic acid has not been expelled in its preparation, a little of it dissolves in the weak acid formed, and crystallises out again on cooling.

*Bismuthous Selenate.*—This was prepared by boiling bismuthous carbonate with selenic acid, and continuing the heating until the excess of acid was expelled. It crystallises in minute white prisms. It is insoluble in water, and is not decomposed by it on boiling, but if selenic acid is present it dissolves. It is also soluble in sulphuric acid on boiling, and readily in hydrochloric and nitric acid. Potash and soda decompose it, uniting with the selenic acid.

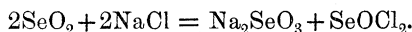
*Platinic Selenate.*—This was prepared by heating platinic chloride with selenic acid until the hydrochloric and excess of selenic acid were expelled. It is a dark-brown body, which dissolves slightly in water on boiling, forming a yellowish-brown solution. It is insoluble in alcohol. It dissolves readily in hydrochloric acid, and leaves metallic platinum on ignition.

#### *The Action of Phosphoric Anhydride upon Selenic Acid.*

When sulphuric acid is heated strongly with phosphoric anhydride sulphuric anhydride is evolved; on the other hand, the effect of heating a mixture of anhydrous selenic acid and phosphoric anhydride to a high temperature is, that selenious anhydride is given off, and not selenic. In order to see if a different reaction occurs between the latter two bodies at a lower temperature, some anhydrous acid was mixed with phosphoric anhydride in a flask, which was then tightly closed and placed in the water-oven. After heating for some time a clear solution was obtained, and the flask was then removed and allowed to stand in the cold. Crystals were slowly deposited, which under the microscope were seen to be transparent cubes. The acid liquid was drained off, and the crystals examined. So far as an analysis could be carried out the result agrees with the view that the body thus obtained is selenic anhydride,  $\text{SeO}_3$ , but the quantity of material at our disposal at the time was too small to admit of its satisfactory separation and examination. We are, however, at present engaged in operating upon larger quantities, and hope, at no distant date, to submit our results to the Royal Society.

*Selenium Oxychloride.*

It may be useful here to mention a reaction, hitherto undescribed, by which selenium oxychloride can be obtained. It consists in distilling a mixture of sodium chloride and selenium dioxide. The reaction is a simple one—



Half the selenium remains as sodium selenite.

III. "On the Wave-length of the chief Fluting seen in the Spectrum of Manganese." By J. NORMAN LOCKYER, F.R.S.  
Received April 6, 1889.

In a paper communicated to the Royal Society in November, 1887, I pointed out that in the spectra of certain classes of heavenly bodies there are several lines and flutings which occur in the low-temperature spectra of meteorites.

In a subsequent paper\* I gave tables showing further that lines occupying nearly the same position had also been recorded in the spectra of auroræ. The coincidences were really surprising, and I therefore suggested that the spectrum of the aurora might in part be due to particles of meteoric dust in the upper parts of our atmosphere.

One of the most constant flutings thus apparently common to the spectra of meteorites, meteor-swarms (nebulae and stars as well as comets), and auroræ is one near wave-length 558. I, therefore, suggested that the remnant of this fluting, which is seen in the spectrum of manganese (whether due to the metal or a compound is unimportant in the present connexion), was the origin of the chief line of the aurora spectrum. I distinctly stated that only small dispersion had been employed of set purpose, and that the wave-lengths given had no claim to great accuracy.

From a detailed discussion of all the published observations available to me,† the suggestion as to the meteoritic nature of the aurora seemed fully justified, both as regards the general characteristics of the spectra and the positions of the lines and flutings observed, but I was particularly careful to point out that the object of my paper was mainly to direct further inquiries.

Dr. Huggins has communicated an interesting paper to the Royal Society,‡ in which he gives the results of some very careful measure-

\* 'Roy. Soc. Proc.,' vol. 43, p. 320.

† 'Roy. Soc. Proc.,' vol. 45, p. 217.

‡ 'Roy. Soc. Proc.,' vol. 45, p. 430.